

EMISSION BAND SPECTRUM OF SeO_2 MOLECULE

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Plate XIV

ABSTRACT. The emission spectrum of pure SeO_2 vapour as excited in a high frequency discharge from an oscillator and in an uncondensed discharge from a transformer, is found to reveal a number of characteristic bands in the region λ 4700 to λ 2750. These bands are diffuse and are attributed to the emitter, the triatomic SeO_2 molecule. About 100 bands in the region λ 4700 to λ 3200 are analysed as belonging to two new systems of SeO_2 molecule arising out of transitions from the deformation vibrational levels of the upper states to symmetric vibrational levels of the lower states. The following are the vibrational constants of the two systems.

	$\nu_{\text{O-O-O}}$	Sym. vib. frequency of lower state	Def. vib. frequency of upper state
System -I.	32145 cm^{-1}	910.5 cm^{-1}	182 cm^{-1}
System -II.	32052 cm^{-1}	911.5 cm^{-1}	182 cm^{-1}

Bands below λ 3200 down to λ 2750 are found to belong to a part of the B - X system of SeO_2 molecule observed previously in absorption.

INTRODUCTION

In our recent investigation on the spectra of the dioxides of selenium and tellurium, it has been found that the emission of pure SeO_2 vapour excited in electrical discharges revealed a characteristic band spectrum consisting of a number of new bands in the visible and near ultraviolet region. The origin and nature of these new bands have been discussed in this paper.

EXPERIMENTAL

Selenium dioxide employed in the present investigation is a white powder which sublimes at 315°C . The substance was perfectly dehydrated before it was introduced into the discharge tube. Spectra were excited by an oscillator of approximately 50 Watt output power at 10 m.c.s. frequency and in an uncondensed discharge from a 10 KV transformer. The oscillator discharge tube was an ordinary pyrex glass tube of 30 cm. in length and 20 mm in diameter. One end of the tube was drawn into an adaptor and was connected to a system of high vacuum pumps. The other flat end was closed by a quartz window. The electrodes drawn directly across the tank circuit of the oscillator, were wrapped

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round the discharge tube. A flowing vapour of the substance was maintained inside the tube by continuous evacuation and by occasional heating with Bunsen flame.

In the case of transformer discharge experiments, a similar discharge tube was employed but provided with two side limbs at 10 cm apart fused with tungsten electrodes to which the high tension of 10KV was applied. In both these discharges the colour of the emission free from usual impurities is deep blue.

Spectra were photographed on Hilger Medium Quartz, Fuess, Hilger's Quartz Littrow and Glass Littrow spectrographs and were recorded on Ilford Special Rapid plates. The times of exposures were of 5 to 10 minutes duration on the low dispersion instruments and of 20 to 30 minutes duration on the high dispersion instruments.

RESULTS

The emission of SeO_2 vapour excited in different electrical discharges revealed a characteristic spectrum of a number of bands in the region $\lambda 4700-\lambda 2700$. Plate XIV, Fig. 1(a) and (b) are the reproductions of the spectra photographed on the medium quartz instrument. The band heads in the region $\lambda 4700-\lambda 3200$ (strip-a) appear diffuse and those below $\lambda 3200$ down to $\lambda 2700$ (strip-b) are sharp and red degraded. Each of these diffuse bands when photographed on high dispersion Littrow spectrographs, was resolved into a number of component heads of different intensities which might correspond probably to the isotopic effect of selenium in the SeO_2 molecule. About 100 band heads in the region $\lambda 4700-\lambda 3200$ were measured on a number of high dispersion plates and the accuracy of the band head data was found to be within the limits of 2 to 3 cm^{-1} .

The wavelength data of these new bands were compared with the band head data of the well known spectra of the diatomic SeO and Se_2 molecules excited under similar conditions. They totally disagree and the spectra of the three molecules appear entirely different from each other. On the other hand, the new bands do not appear to possess the characteristic rotational structure, even when photographed on the high dispersion instruments, which should be the case if they belong to the diatomic SeO molecule. On the basis of this experimental evidence, the 100 bands in the region $\lambda 4700-\lambda 3200$ obtained in the present investigation, could tentatively be assigned to the triatomic emitter SeO_2 molecule. The sharp red degraded bands in the region below $\lambda 3200$ to $\lambda 2700$ were found to belong to a part of the previously known $B-X$ system of SeO_2 observed in absorption by Duchesne and Rosen (1941).

ANALYSIS OF THE BANDS

Already three systems, namely, A, B and C, are observed (Choong Shin Piaw, 1938 ; Duchesne and Rosen, 1947) in absorption of SeO_2 vapour in which B and C

TABLE I
Vibrational analysis of system I

v_1'	v_2''	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0.	32145	31234	30332	29426	28535	27645	26762	25883	25010	24144	23289	—	—	21599	—
1.	32326	31416	30511	29614	28713	27833	26946	26068	25195	24323	23470	22617	—	—	—
2.	—	—	30695	29798	28889	28007	27125	26252	25370	24501	23651	22795	22795	—	—
3.	—	—	—	29975	29068	28184	27301	26410	25547	24681	23822	—	—	—	—
4.	—	—	—	30148	29248	28366	27471	26592	25728	24860	23992	—	—	—	—
$\Delta G(v_2'')$		910.5	903.5	900	900	884	884	880	871	868	857	845.5	—	—	—

TABLE II
Vibrational analysis of system II

v_1'	v_2''	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0.	32052	31143	30226	29339	28446	27552	26668	25790	24919	24054	23200	22356	21520	—	—
1.	32234	—	30423	29523	28626	27732	26848	25973	25097	24238	23379	22537	21703	—	—
2.	—	31499	30601	29699	28804	27913	27032	26152	25277	24412	23558	22710	21882	21053	—
3.	—	—	30779	—	28982	28089	27213	26327	25456	24589	23736	22888	—	—	—
4.	—	—	—	—	29161	28270	—	26503	25633	24754	23910	—	—	—	—
$\Delta G(v_2'')$		909	902.5	900	895	893	881	880	873	867	853	8455	833	829	—

occurring in the regions $\lambda 3400-\lambda 2200$ and $\lambda 4500-\lambda 3400$ respectively, are more extensive. There are possibilities that the present emission bands in the region $\lambda 4700-\lambda 3200$, might either belong to system *C* or form an extension of system *B*. No agreement was found between the wave-length data of these emission bands and the absorption bands of C-X system occurring in this region. Attempts made to extend the analysis of B-X system to include the present emission bands yielded no satisfactory analysis. The emission bands above $\lambda 3200$ appear diffuse whereas the bands below $\lambda 3400$ belonging to the B-X system are sharp and red degraded. As such, the series of emission bands in the region $\lambda 4700-\lambda 3200$ cannot be attributed to either of the two systems *B* and *C* and are to be considered as forming one or more new systems of SeO_2 molecule.

The whole series of new bands in the region $\lambda 4700-\lambda 3200$ are analysed as belonging to two new overlapping systems to each of which every alternate band belongs. These two systems are designated here as Systems I and II and their vibrational analyses are presented in Tables I and II.

In both the systems, several characteristic long lower state progressions are developed. Some of these prominent progressions are marked in Plate XIV, Fig. 1(a) & (b). An average difference of 910 cm^{-1} is observed between the successive bands near origin of the system in each progression of the two systems. This frequency of 910 cm^{-1} can be identified with or can be considered as a similar one to the previously known symmetric vibrational frequency $\omega''_2 = 910\text{ cm}^{-1}$ for the ground state of SeO_2 molecule derived from the absorption work of C-X system by Duchesne and Rosen (1947)

For each system, only four upper state progressions are formed with a characteristic difference of about 180 cm^{-1} between the successive bands. The low value of this frequency in each system suggests that this has to be identified as the deformation vibrational frequency of the corresponding excited states of SeO_2 molecule. Thus, the transitions observed in the two systems are from the vibrational levels of the upper states with deformation frequency $\omega'_1 = 182\text{ cm}^{-1}$ to the vibrational levels of lower states with symmetric frequency $\omega''_2 = 910\text{ cm}^{-1}$.

The vibrational constants for the two emission systems as obtained from the analysis are as follows.

	$\nu_{0,0-0}$ cm^{-1}	Symmetric vib. frequency of the lower state ω''_2	$X''_2\omega'_2$	Def. vib. frequency of the upper state. ω'_1
System I	32145	910.5 cm^{-1}	3.0 cm^{-1}	182 cm^{-1}
System II	32052	911.5 cm^{-1}	2.5 cm^{-1}	182 cm^{-1}

Since, the corresponding average $\Delta G(v''_2)$ values of the lower state progressions are almost equal in the two systems, they might be considered of having a common

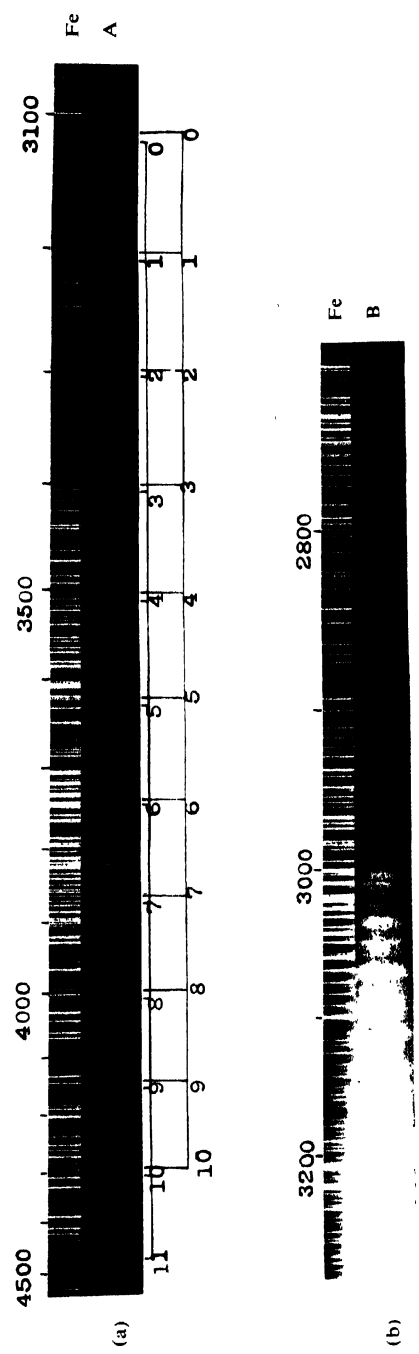


Fig. 1 (a) Emission spectrum of SeO₂ Vapour (λ 4500 – λ 3200).
(b) Emission spectrum of SeO₂ Vapour (λ 3200 – λ 2700).

lower state. However, it is difficult to conclude whether this common lower state is the same as the normal state of SeO₂ molecule, since these bands are not observed in absorption.

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